Preparation and Characterization of High Purity CdTe Single Crystals(高純度CdTe単結晶の作成と評価)

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論文内容要旨

Chapter 1 Introduction

Among binary II－VI compound semiconductors, CdTe is supposed to be the only one having applicably high both n- and p-type conductivity. Although a quite wide application of this material has been realized, a full understanding of the behavior of some active point defects in CdTe has not been achieved, and a good control of the electrical and optical properties of this material remains difficult, mainly because the currently available CdTe single crystals are lacking in quality. Either to advance the fundamental researches or to improve the performance of this material, the improvement of the crystal quality has become more and more significant and compelling.

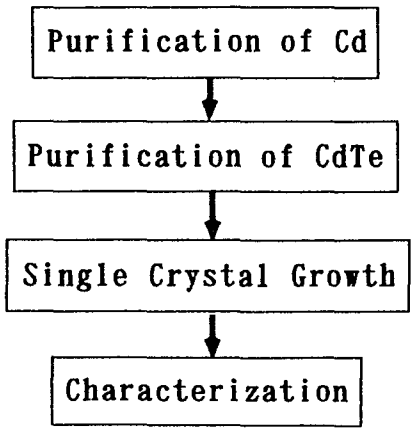

Fig. 1 Process for the preparation and characterization of high purity CdTe single crystals.

The present research, therefore, is directed at preparing high purity CdTe single crystals, from the purification of starting material Cd to the crystal growth and characterrization of CdTe. Figure 1 shows the experimental process. Objectives of this work include also the investigation of the electrical and optical properties of CdTe and the elucidation of the behavior of some impurities and native defects as well as their complicated interactions.

Chapter 2 Preparation of High Purity Cd

Since the purification of Cd is far more difficult than that of Te, the purity of Cd becomes the key factor improving the purity of resulting CdTe crystals. High purity Cd is obtained by Overlap Zone Melting (OZM) method performed in high purity hydrogen stream, following twice Vacuum Distillation (VD). The purity of

resulting Cd is evaluated, in each purification step, with Glow Discharge Mass Spectroscopy (GDMS) and Residual Resistivity Ratio (RRR) . In order to get a correct interpretation of the RRR values, the specimen for RRR measurement is annealed under a fully examined condition (373K, Vacuum, 4 hours). VD process shows significant purification effect on Ni, Cu, Co and Pb, whileSi, Cl, Ni, Zn and Tl can be efficiently reduced by OZM. The total concentration of residual impurities of the finally obtained Cd, the center part of OZM ingot, is below 0.1 mass ppm, and the RRR value is higher than 20000 (Fig. 2) .

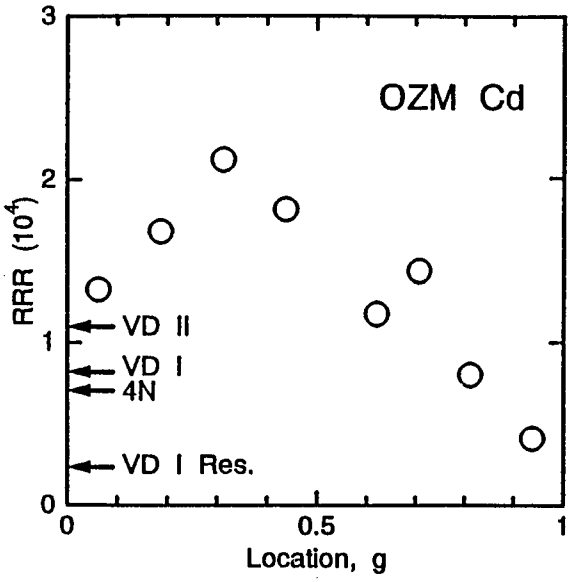

Fig. 2 RRR values of overlap-zone-melted Cd ingot, along with those of VD samples.

Chapter 3 Purification and Crystal Growth of CdTe by Vertical Bridgman Method (Normal Freezing)

High purity CdTe single crystals are grown by the conventional vertical Bridgman (VB) method using the high purity Cd (OZN Cd) as well as 6 N Cd (VD II Cd) for comparison. The purity difference of starting Cd explicitly replicates in resulting CdTe crystals, as shown in Fig. 3. Effective purification of CdTe is achieved during the normal freezing of VB growth, owing to the segregation of residual impurities. The purest part of the crystal ingot, verified by photoluminescence study, is used as the source of the subsequent PVT growth.

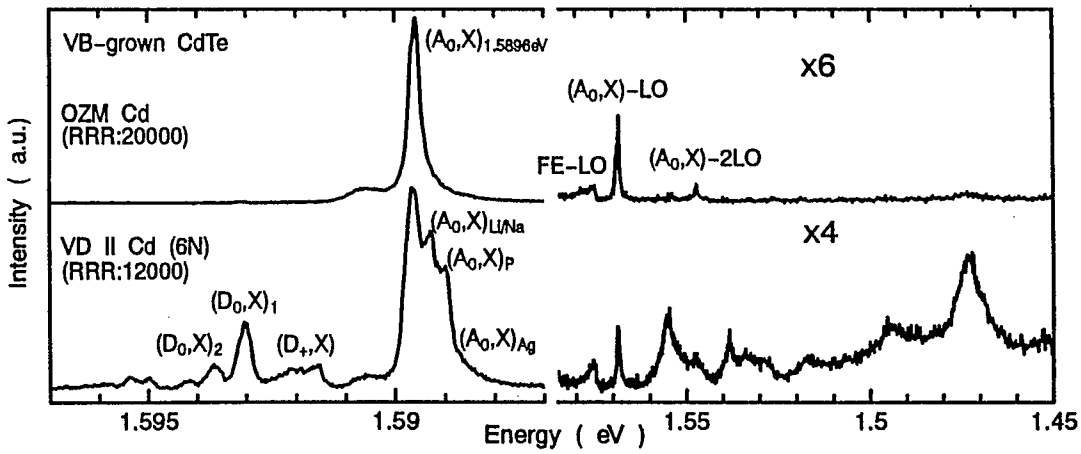

Fig. 3 Typical 4.2K PL spectra of VB-grown CdTe single crystals.

Chapter 4 Growth of High Quality CdTe Single Crystals by Physical Vapor Transport

High quality CdTe single crystals are grown by Physical Vapor Transport (PVT) under a controlled vapor composition by a Cd reservoir. Some metallic elements, known as the especially detrimental impurities, are efficiently reduced. PL spectrum of PVT-grown CdTe crystal is shown in Fig. 4. The concentration of isolate neutral donor derived from the Cyclotron Resonance (CR) study is $5 \times 10^{14}\,cm^{-3}$, and the electron mobility at 4.2K is $2.5 \times 10^5 cm^2/Vs$, the highest reported value, showing high crystal perfectness. The IR transmittance of the PVT-grown single crystals is much improved, which indicates that the Te precipitates, commonly present in the VB-grown CdTe crystals, are much inhibited in the PVT growth. The improvement of the PVT growth ampoule is demonstrated very effective for reducing the oxidation of source materials and the incurrence of

volatile impurities and, consequently, improving the growth rate and reproducibility.

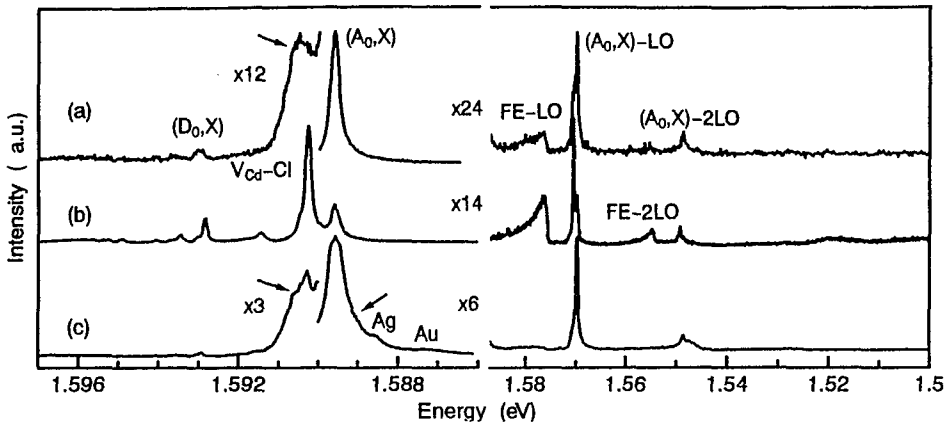

Fig. 4 PL spectra of CdTe : (a) VB-grown crystal, (b) PVT-grown crystal and (c) PVT residue.

Chapter 5 Aging Behavior of Some Residual Impurities

The emission intensities of (D_0, X) and (A_0X) related to Ag, P, and Li or Na in the PL of VB-grown CdTe crystals are found to decrease significantly with room temperature aging, as shown in Fig. 5. This observation, in the case of metallic impurities, is attributed to the instability of these impurities occupying Cd-sites, that is, these impurities migrate from Cd-sites to the interstitial sites during the aging. The products of this process, Cd vacancy (V_{Cd}) and interstitial metallic elements (M_i), further associate with shallow donors and acceptors, respectively, which is account for the aging behavior of the emissions of (D_0, X) and $(A_0, X)_P$. Involved processes are described by

$$M_{Cd} \text{ -------} > V_{Cd} + M_i,$$

$$V_{Cd} + \text{Donor } \text{--------} > V_{Cd} - D,$$

and $$M_i + \text{Acceptor } \text{-------} > M_i - A.$$

This aging observation and interprettion is confirmed by Ag-doping experiments.

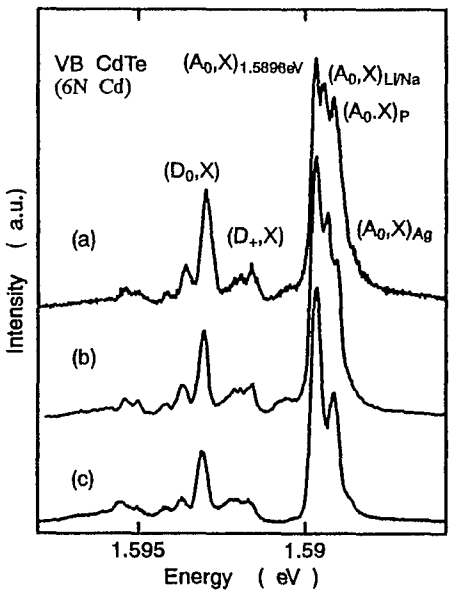

Fig. 5 PL spectra of VB-grown CdTe crystals after aging for (a) one month, (b) five months and (c) one year.

Chapter 6 Electrical and Optical Properties of CdTe Single Crystals Depending on Cd-annealing

The electrical and optical properties of CdTe are examined on the crystals grown by VB using OZM Cd as the starting materical. The photo-luminescence, infrared transmittance (IR) and conductivity properties are investigated regarding Cd-annealing. With the increase of Cd-pressure, the conductivity of annealed CdTe crystals changes from p-type to n-type, and the concentration of electron increases significantly. It is mainly attributed to the appearance of Cd_i and the release of the donor involved in the complex V_{Cd}-D. The infrared extinction is dominated by carrier absorption the

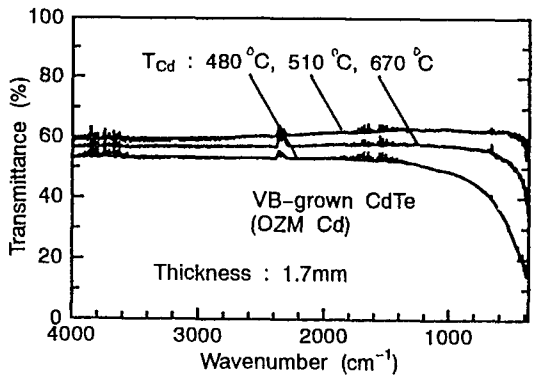

Fig. 6 IR transmission spectra of CdTe cry-s tals annealed at 700 °C for 3 days under various Cd pressures (Cd-reservoir temperatures, T_{Cd}).

lower energy and by precipitate scattering at higher energy. Figure 6 shows the annealing dependence of IR transmittance of CdTe. Separated estimation of the scattering and absorption is approached. The results show that the electrical and optical properties of CdTe crystals can be controlled by the annealing in the vapor of a constituent element.

Chapter 7 Origin of the Emission Line of (A_0, X) at 1.5896eV

The origin of the emission line of (A_0, X) at 1.5896eV, commonly observed as the dominant line in the PL spectra of CdTe, is explored. Experimental results of aging, Cu-doping and Cd-annealing reveal that this line actually contains two emissions. The emission with higher relates to a V_{Cd}-related defect ; the other one, to Cu_{Cd}. The energy difference between them is less than 0.1 meV. The V_{Cd}-related defect is aging-stable, but its nature remains unclear. On the other hand, Cu_{Cd} is supposed showing aging behavior at room temperature, like Ag_{Cd}, Li_{Cd} and Na_{Cd}.

Chapter 8 Summaries

High quality CdTe single crystals are grown by improved PVT following the synthesis and purification by VB process,using the highly purified Cd. Electrical and optical properties of high purity CdTe depending on Cd-annealing are investigated. Elucidation of the behavior of some point defects is approached.

審 査 結 果 の 要 旨

CdTeは赤外線検出器用材料であるCdHgTeの基板として応用され，また室温で動作する放射線検出器用材料としても注目されている。しかし，他のII－VI族化合物と同様，現在のCdTe単結晶の純度は不十分で，その特性を左右する不純物と固有欠陥の挙動は明らかにされているとは言い難い。本論文は素材純度の高純度化から出発して，従来にない高純度かつ高品位のCdTe単結晶を成長させると共に，不純物の添加および成分分圧下の熱処理を加え，その電気的・光学的特性の変化を調べることにより，不純物および固有欠陥の挙動に関する知見を得たもので，全編8章よりなる。

第1章は緒論であり，本研究の背景と目的を述べている。

第2章では，真空蒸留と重複帯溶融法により，素材であるCdの精製を行い，総不純物料が0.1mass ppm以下の高純度Cdを得ることに成功している。

第3章では，ブリッジマン法によってCdTe単結晶の成長を行い，素材の高純度化の効果が大きいことを確認すると共に，不純物の偏析現象を明かにした。

第4章では，前章で得た単結晶の高純度部をソースとして，気相輸送法によって高品位CdTe単結晶を成長させた。成長アンプルを改良することによって原料封入時の汚染を低減し，従来の気相成長で難しい問題であった成長速度の向上と再現性の改善を果たした。さらに得られた単結晶が高純度かつ高品位であることをフォトルミネッセンス，赤外線透過スペクトルの測定および光励起サイクロトロン共鳴の実験から明かにしている。

第5章では，不純物の室温時効挙動を不純物の束縛励起子発光強度の経時変化から観察し，不純物の存在位置不安定性を確認している。また，個々の不純物の関与する発光強度変化を矛盾無く説明出来る複合欠陥の形成モデルを提案し，その妥当性をAgの添加実験によって確認している。

第6章では，高純度単結晶を用い，Cdの雰囲気中での熱処理に対する電気的および光学的特性変化を調べ，固有欠陥制御の可能性を明かにした。さらにCdTe単結晶の赤外線透過スペクトルの解析から析出物密度とキャリア濃度を評価できることを明かにしている。

第7章では，as-grown結晶とCu添加結晶を用い，Cd雰囲気処理に対する発光強度変化を詳細に調べることによって，CdTeの主な発光線である1.5896eVの束縛励起子発光の起源を調べ，Cd空孔およびCuの2種類のアクセプターが関与した発光であることを初めて明かにした。

第8章は結論である。

以上要するに本論文は，高純度CdTe単結晶の成長方法を確立し，成長結晶を試料としてCd雰囲気処理と不純物添加を行い電気的・光学的特性を評価し，不純物と固有欠陥に関する知見を得，その制御の可能性を明かにしたもので，材料光学の発展に寄与するところが少なくない。よって，本論文は博士（工学）の学位論文として合格と認める。